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ADSORPTION, MOBILITY AND ORGANISATION OF ORGANIC  
MOLECULES AT CLAY SURFACES PROBED BY PHOTOPHYSICS AND  
PHOTOCHEMISTRY

SIXTH INTERIM REPORT

15 june 1989

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UNITED STATES ARMY

EUROPEAN RESEARCH OFFICE OF THE U.S. ARMY  
LONDON, ENGLAND

DAJA 45-87-C0006

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TABLE OF CONTENTS

- THIS REPORT CONTAINS RESULTS FROM
- A. Cluster formation of detergents on the clay surface.
  - B. Adsorption of aromatic compounds on colloidal silica.
  - C. Study of the fluorescence decay of molecules adsorbed on surfaces.
  - D. Conclusions
  - E. References



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## A. CLUSTER FORMATION OF DETERGENTS ON THE CLAY SURFACE

### 1. Introduction

The adsorption of organic molecules on a clay surface can be studied by means of specifically designed fluorescent probes (1-7). Indeed, by studying the photophysical properties of the adsorbed probes, information on the adsorption and distribution of organic molecules can be obtained.

As reported previously cationic pyrene derivatives have been used to examine the nature of the adsorption process, since these molecules are strongly bound to the negatively charged clay particles. Also, the influence of co-adsorbed cationic surfactants on the photophysical properties of the adsorbed probe molecules has been investigated.

It was found that the adsorbed molecules form clusters in aqueous suspensions.

In our previous report we suggested that the hydrophobic interaction between the adsorbed molecules is an important driving force of cluster formation. In this contribution, a more detailed study of this cluster formation in aqueous suspensions is presented.

At low loadings, information on the size of the detergent clusters on the clay surface could be obtained both by fluorescence quenching and by polymerization of specifically designed detergent.

Due to the hydrophobic interactions between the detergent molecules double layers are formed at higher detergent concentration. Recently a serie of experiments were started to try to determine the nature and size of this double layer.

### 2. Determination of the size of the detergent clusters

#### 2.1. Polymerization of methacryloyloxyethylmethyldidodecylammonium chloride (DDMEMEC) on a Laponite surface in aqueous medium

In the previous report the polymerization of DDMEMEC, adsorbed on Laponite surface, was described. DDMEMEC was polymerized directly by irradiation at 250 nm (in a quartz cell) in the absence of any initiator. The major problem was the separation of the obtained polymer from the clay surface. It was however possible to desorb the

polymer by chemical modification of the latter. A desorption could be realized by basic hydrolysis of the ester group of the detergent.

The polymer-clay mixture was treated with a 3M NaOH solution and refluxed at 100 °C during 24 hours.

This basic hydrolysis results in the formation of polymethacrylic acid, which is soluble in basic media. The clay particles, together with the ammonium residues, are precipitated by centrifugation (4000 rpm )

After separation, the polymer is precipitated from the supernatant solution by adding 3M HCl .

The I.R.spectrum of the obtained polymer is identical to the I.R. spectrum of the polymethacrylic acid (8). The molecular weight of this polymer was assessed by viscosity measurements ( fig. 1 ) in NaOH solution (2M) at 25 °C using the equation

$$[\eta] = K M^{\alpha} \quad (I)$$

Where  $[\eta]$  is the intrinsic viscosity,  $K = 42.2 \cdot 10^{-5}$  dl/g, and  $\alpha$  is 0.64 (9).

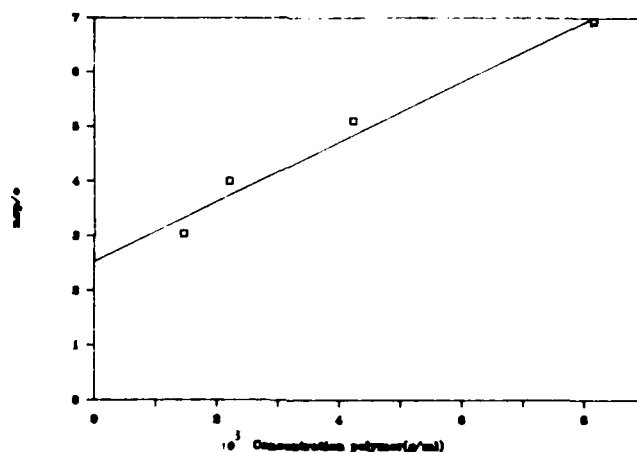


fig. 1.1 specific viscosity in function of polymer concentration

The obtained molecular weight corresponds to 7 monomer units. This is the clustersize for a detergent concentration which amounts to 27% of the C.E.C. of Laponite.

This result suggests that the detergent clusters on the clay surface are rather small.

## 2.2. Fluorescence Quenching.

As the detergents form clusters on the clay surface, an attempt was made to describe the fluorescence decay of adsorbed P3N molecules in the presence of detergent using decay laws used in the analysis of fluorescence quenching in micellar media (10,11).

These measurement were performed on a Laponite suspension in the presence of CTAC molecules. The fluorescence decay of a Laponite suspension with a total coverage of 12 %, using a ratio [ P3N ] / [ CTAC ] of 200 was analysed.

Even at this ratio an excimer emission at 480 nm is observed. The fluorescence decay of P3N, monitored at 378 nm could be fitted to the following equation:

$$\Phi(t) = A_1 \exp(-A_2 t) - A_3 (1 - \exp(-A_4 t)) \quad (II)$$

This equation describes the fluorescence quenching in micellar media (11,12) and allows, within certain experimental conditions, the determination of the aggregation number of the detergent clusters. The values obtained by single curve analysis are shown in table 1.

The intermolecular excimer formation is, in the presence of CTAC molecules a dynamic quenching process.

Indeed, the fluorescence decay of the excimer emission shows a growing-in. It should be noted that the excimer emission of P3N adsorbed on a clay surface in the absence of detergent molecules is not due to a dynamic quenching. (6)

This phenomenon was also observed by de Mayo et al. (13) for the intermolecular excimer formation of pyrene adsorbed on a silica surface. In the absence of co-adsorbed molecules the excimer formation was a static process, while after addition of alcohols the excimer formation was shown to be a dynamic process.

Assuming no exchange of excited P3N molecules between the detergent clusters, the physical meaning of the parameters  $A_1$  to  $A_4$  can be expressed as :

$$A_1 = I_0 \quad (III)$$

$$A_2 = k_0 \quad (IV)$$

$$A_3 = [P3N] / [M] \quad (V)$$

Where  $[M]$  is the cluster concentration,  $I_0$  the fluorescence intensity at time zero after excitation,  $k_0$  the reciprocal of the fluorescence lifetime of P3N molecules which are not quenched, and  $k_q$  a first order rate constant related to the excimer formation (13).

From these parameters the aggregation number of the detergent clusters can be calculated using the following equation :

$$N_{ag} = A_3 [CTAC] / [P3N] \quad (VI)$$

An second concentration of P3N ( $7.8 \cdot 10^{-7}$  M) was investigated maintaining the CTAC concentration constant ( $4 \cdot 10^{-5}$  M)

In table 2 the results of a global analysis at two different concentration of P3N ( $2 \cdot 10^{-7}$  M,  $7.8 \cdot 10^{-7}$  M) are given. An average aggregation number of 25 was obtained.

The higher aggregation number for CTAC at a lower detergent concentration than for DDMEEC suggest a strong detergent dependence of the clustersize.

In view of the success of this approach, it will be further extended to other systems to determine the limitations of this model.

### 3. Formation of surfactant double layers on the Laponite surface

Bilayer adsorption on Laponite surface by adding consecutively both cationic and anionic detergents to the clay suspension was investigated. The surfactants used were methacryloyl-oxyethylmethyldidodecyl ammonium chloride (DDMEEC), a positively charged detergent, and dodecyl sulfate sodium salt (SDS), a negatively charged detergent.

A fluorescent probe, 1-methylpyrene, was used.

The aim of this study is to get information on the aggregation number

table 1 : Recovered parameter values and goodness of fit for single curve analysis

[CTAC] 10 <sup>5</sup> (M)	[P3N] 10 <sup>7</sup> (M)	$\lambda$ (nm)	P <sub>1</sub> *10	P <sub>2</sub> *10 <sup>-2</sup>	P <sub>3</sub> *10	P <sub>4</sub> *10 <sup>-1</sup>	P <sub>5</sub> *10 <sup>-1</sup>	$\chi^2$	Z $\chi^2$	Nagg
4	2	380	6.719	2.021	1.475	5.685	1.560	1.059	0.655	30
		385	6.261	2.044	1.122	3.129	1.560	1.103	1.159	22
		390	6.512	2.039	1.529	5.347	1.560	1.135	1.508	31
4	7.8	378	8.079	1.977	4.002	9.446	1.560	1.088	0.985	21
		385	8.497	1.964	4.453	1.036	1.560	1.209	2.338	23
		390	9.101	1.953	4.659	1.123	1.560	1.182	2.041	24

Table 2 : Recovered parameter values and goodness of fit for global analysis

[CTAC] $10^5(M)$	[P3N] $10^7(M)$	$\lambda$ (nm)	$P_1 \times 10$	$P_2 \times 10^{-2}$	$P_3 \times 10$	$P_4 \times 10^2$	$P_5 \times 10^{-1}$	$Z\chi^2$	$Z\chi^2_{glob}$	Nagg
4	2	380	6.585	2.035	1.348	4.616	1.560	1.323	2.651	27
		385	6.448	2.035	1.348	4.616	1.560	1.760		
		390	6.409	2.035	1.348	4.616	1.560	1.795		
4	7.8	378	8.446	1.965	4.328	1.038	1.560	1.800	3.786	23
		385	8.437	1.965	4.328	1.038	1.560	2.375		
		390	8.796	1.965	4.328	1.023	1.560	2.676		



of the double layer.

To 50 ml of a Laponite suspension (1g/l), 10 ml of DDMEEC ( $2.2 \cdot 10^{-3}$  M) was added, due to the reduction of the charge of the clay particle by the binding with the cationic detergent molecules the particles are not longer stabilized and flocculation takes place.

To the floc 20 ml of  $2 \cdot 10^{-3}$  M SDS was added, and the particles are redispersed which indicates a double layer was formed.

0.2 ml of methylpyrene  $8.4 \cdot 10^{-6}$  M / dichloromethane solution was placed into a 5 ml volumetric flask, and the solvent was purged away with argon.

5ml of the clay suspension containing the detergent double layers was then added. A preliminary quenching study with KI as a quencher indicates a distribution of KI over the organic and water face.

Further study using organic quenchers is in progress.

## B. ADSORPTION OF AROMATIC COMPOUNDS ON COLLOIDAL SILICA

### 1. Introduction

The photophysics and photochemistry of organic molecules adsorbed on oxide surface have been studied in recent years because of their potential use as diagnostic probes of surface adsorbate interactions. There are many varieties of colloidal silica which as they are optically clear, provide convenient systems for the study of  $\text{SiO}_2$  water interface.

The colloidal  $\text{SiO}_2$  particles can be of various dimensions from radii of about 10 Å upward; the particles may also be porous (14,15). The surface of the particles is charged, via ionization of the surface silanol groups and via adsorption of ions.

Silica is unique among colloids in its surface charge-pH and total double-layer capacitance behavior<sup>(16)</sup>. These factors are much higher than on other colloids for which a suitable theory has been developed based on the Nernst equation. Sears<sup>(17)</sup> showed that at a given pH, the number of charges per unit area of silica surface does not depend on the particle size. A site-binding model of the oxide-water interface was presented by Yates<sup>(18)</sup>, in which adsorbed counterions form double layers with ion pairs which discrete charged surface groups. Because of the negative nature of the silica colloid at high pH, the colloidal  $\text{SiO}_2$  does not contain groups (e.g.  $\text{SiOH}$ ) which can adsorb uncharged molecules such as arenes etc. However, cationic species can adsorb to the anionic  $\text{SiO}_2$  surface.

In this study, a probe molecule 3-(1-pyrenyl)propyl trimethylammonium bromide P3N has been used to investigate the nature of colloidal silica particles in water. This probe is cationic and can adsorb on the colloidal silica particles. Pyrene probes are widely used because of their ability to form an excimer and their long singlet lifetime.

The effect of change in pH and water to silica (w/s) ratio on the emission of P3N and quenching measurements using two types of commercial silica colloid Ludox<sup>R</sup> were studied; one of them is WP 35% (wt %) with specific surface area of 140 m<sup>2</sup>/g, an average particle diameter of 22nm and a viscosity of 4cp and a PH of 10.7. The surface is modified with aluminate ions by replacing some of the surface silicon atoms with aluminum atoms, this creates a fixed

negative charge independent of pH. The concentration (35%) includes  $\text{SiO}_2 + \text{Al}_2\text{O}_3$ ; the second sample used is HS-40% characterized as 40%  $\text{SiO}_2$  by wt%, a specific surface area of  $230 \text{ m}^2/\text{g}$ , an average particle diameter of 12 nm ; a viscosity of 20cp and a pH of 9.7 for a solution of 40%. The surface of HS is not modified.

## 2. Effect of silica concentration

The most interesting behaviour was observed when water/silica ratio was the tested parameter. Fig. 2 shows the w/s effect on the emission of the probe in WP colloidal solution. The fluorescence spectra of the probe show that there is no excimer formed in water at the concentration used ( $10^{-6}\text{M}$ ). In the case of silica WP 35%, it was found that there is a small excimer emission by dilution to 20% and the excimer increases with decreasing concentration of  $\text{SiO}_2$ . In the case of the silica colloid HS-40%, it was found that by dilution from 40% to 10% there is no difference between the fluorescence spectra on silica and in water and no excimer is formed even when the concentration of the probe increases from  $10^{-6}\text{M}$  to  $10^{-5}\text{M}$  (in the case of HS-40%).

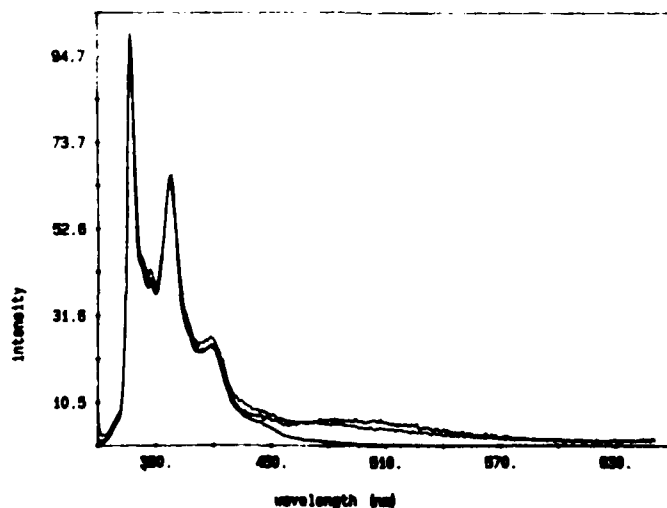


fig. 2 : emission spectra of P3N ( $10^{-6}$ ) in water (a), on .1 % silica WP (b) and on 20 % silica WP (c)

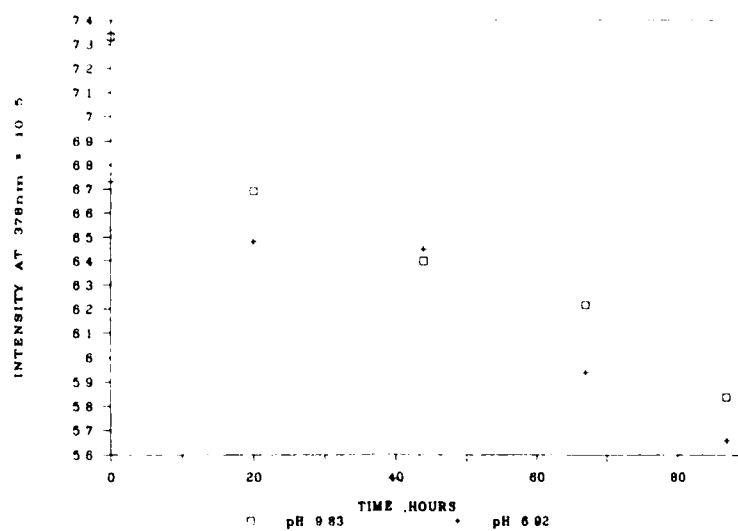


fig. 3 : intensity of emission at 378 nm in function of time

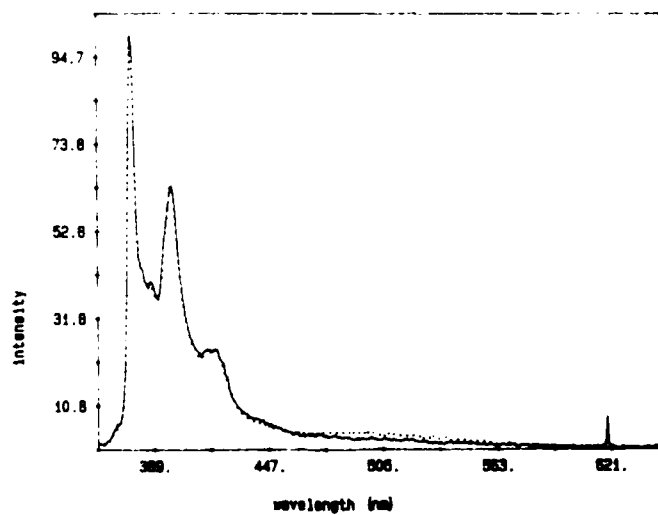


fig. 4 : emission spectra of P3N on .1 % silica WP (a) and on 20 % silica WP (b). The pH was kept constant at 10.35

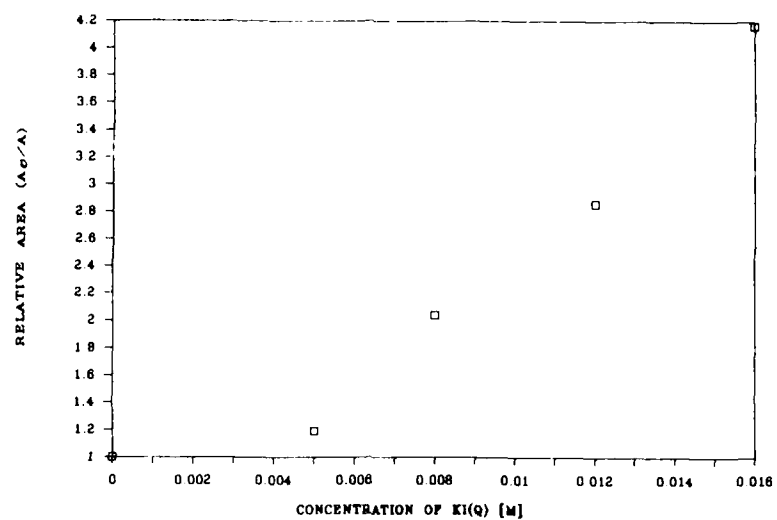


fig. 5 : Stern Volmer plot for the quenching of P3N with KI on silica HS

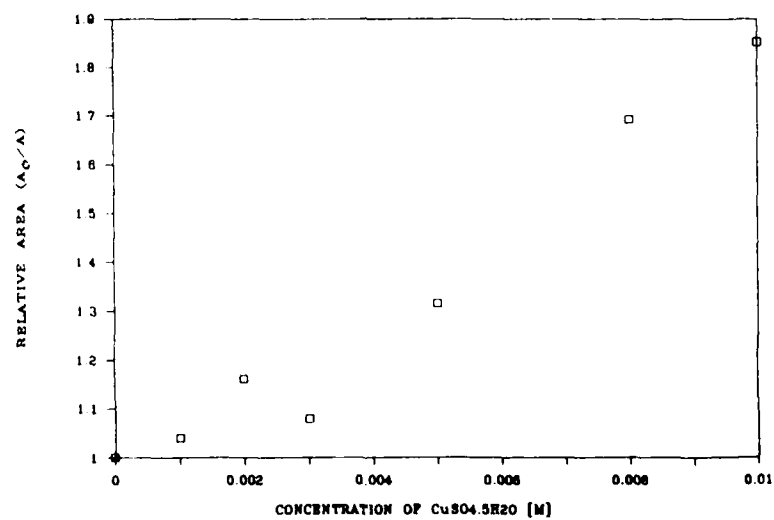


fig. 6 : Stern Volmer plot for the quenching of P3N with CuSO<sub>4</sub> on silica HS

This can be explained by considering the difference in surface area of HS and WP colloidal silica. Because the surface area of HS ( $230\text{m}^2/\text{g}$ ) is larger than that of WP ( $130\text{m}^2/\text{g}$ ), the surface available for adsorption in the case of HS is larger than that in the case of WP, and we consider this to be the reason why excimer is formed in WP colloidal solution and not in HS at the same silica percentage (20%). On the other hand, the increase of excimer with decreasing percentage of  $\text{SiO}_2$  in the case of WP colloid seems logical because the available surface decreases and the probability for excimer formation increases.

### 3. Effect of pH on the adsorption of P3N

In order to study the effect of pH on the adsorption of the probe on silica suspensions of HS in water (20%) were prepared with different pH values varying between 9.83 and 3.28 and the effect of pH on the intensity of fluorescence spectra in function of time was studied. Special attention was given to the change from sol to gel at low pH values. It was found that at  $\text{pH}=5.29$  and lower, silica gel formed after about 50 hours but there is no gel formed at  $\text{pH}>6$  at that time. In the pH range from  $\text{pH}=9.83$  till  $\text{pH}=7.54$  the intensity of emission decreases with time (fig. 3). The reason for this behaviour is not yet clear. In the case of the WP colloidal solution two sets of experiments were carried out. In the first set the concentration of  $\text{SiO}_2$  in the solution was changed keeping pH constant at 10.35, in the second set the concentration of  $\text{SiO}_2$  was altered without adjusting the pH ( $\text{pH}=10.4$  for 20% and 8 for 0.1%) (fig 4). There is excimer formation in both cases and the excimer intensity is higher in the second case.

### 4. Quenching of P3N in colloidal solution

Quenching studies of the excited P3N by anionic ( $\text{I}^-$ ) and cationic ( $\text{Cu}^{++}$ ) quenchers was carried out in colloidal silica HS at concentration 10%  $\text{SiO}_2$  by weight using P3N concentration  $10^{-6}\text{M}$ . No excimer is observed at this concentration in the colloidal solution. The solutions were prepared by diluting a silica HS-40% to 20%. From this solution 2.5ml were placed in 5 ml volumetric flask the probe and the quencher were added the flask was completed to get the same

probe concentration  $10^{-6}M$  and 10% silica with different quencher concentration. The measurements were carried out directly after preparation and after one day to see the effect of addition of ions (anions, cations) on gelation and on the rate of quenching. No linear Stern Volmer plots could be obtained (fig 5, fig 6). This is probably due to a distribution of the quencher over the water and the silica surface. It was found that in the case of  $I^-$ , after one day, at a concentration of  $1.5 \cdot 10^{-2}M$   $I^-$  silica gel was formed, at a concentration of  $1.2 \cdot 10^{-2}M$  no gelation took place. We did not find any gelling with the  $Cu^{++}$  ion at these concentrations. In the case of KI, the  $Na^+$  ions (counterions of silica colloid) and  $K^+$  coagulate the silica more efficiently than the  $Cu^{++}$ . The  $K^+$  ions will act as bridges between particles while the  $Cu^{++}$  exist at that pH as a complex (20).

Single photon timing measurements will be performed in order to calculate the quenching rate constant and the measurements will be repeated in colloidal WP for comparison.

### C. STUDY OF THE FLUORESCENCE DECAY OF MOLECULES ADSORBED ON SURFACES.

#### 1. Introduction.

In general the interpretation of the fluorescence decays of molecules adsorbed on various surfaces (silica, alumina, zeolites, monolayers, clays) is not unambiguous. The time-dependent fluorescence of the organo-clay systems, has also been studied. Several functions have been used to describe the fluorescence decays of adsorbed probe molecules on a clay surface. : one-exponential (1), two-exponential (3), Poisson distribution of lifetimes (5), three-exponential (21).

Adsorbed molecules aggregate on the clay surface. This means that besides monomers, several aggregates (dimer, trimer, ...) are present on the surface. Energy transfer from a single monomeric molecule to the aggregates can thus occur. In addition, these aggregates can form excimers upon excitation. Therefore a very complicated fluorescence decay can be expected.

The distribution of the adsorbed molecules can be changed by co-adsorbing detergent molecules with a sufficient chain length,.

As reported previously the aggregation of the probe molecules decreases with increasing detergent concentration.

The fluorescence decay of the pyrene probe becomes less complex when detergent molecules are co-adsorbed. One possible approach is to use a two-exponential function to fit the fluorescence decay. Besides the monomer lifetime, a short decay time is observed. The contribution of the short decay time decreases with increasing detergent concentration. The fluorescence decay becomes thus more and more one-exponential with increasing detergent concentration but, even at the highest detergent concentration a multi-exponential function is needed to describe the fluorescence decay.

In a certain region of concentration one can successfully apply micellar kinetics to describe the fluorescence decay, as is shown earlier in this report.

When there is no detergent co-adsorbed the fluorescence decay of the adsorbed probe is very complicated. Here a three-exponential function is sometimes used to fit the decay. Short decay components are found besides the monomer fluorescence lifetime. These short decay components are usually ascribed to the aggregates.



However there exist no underlying model to explain this three-exponential behaviour.

## 2. Simulations of fluorescence decays using the fractal concept

### 2.1. Introduction

A new approach to the problem of the fluorescence decay of molecules adsorbed on surfaces is offered by the use of the expression developed by Klafter and Blumen which describes the Förster energy transfer in a fractal environment.

The notion "fractal" was first used by Mandelbrot to describe geometrical structures whose dimensions have non-integer values.<sup>(22)</sup> Fractals have the potential to describe a multitude of irregular structures. All of these structures are then characterized by a fractal dimension  $D$ . With the aid of this fractal dimension it is possible to distinguish between different irregular structures in a more or less quantitative manner.

As mentioned before an expression was derived by Klafter and Blumen for the Förster energy transfer from a donor molecule to a set of acceptor molecules which are randomly distributed on a fractal surface.<sup>(23)</sup>

$$\Phi(t) = \exp[-t/\tau_D - \gamma_A(t/\tau_D)^\beta] \quad (\text{VII})$$

$$\text{where } \beta = D/s \quad \text{and} \quad \gamma_A = x_A(d/D)V_d R_0^D \Gamma(1-\beta)$$

$\tau_D$  is the lifetime of the donormolecule and  $s$  is the order of the multipolar interaction (6 in the case of dipolar interactions);  $x_A$  is the fraction of fractal sites occupied by an acceptor;  $d$  and  $D$  are the Euclidean and fractal dimension respectively;  $R_0$  is the critical transfer distance;  $V_d$  is the volume of a unit sphere in  $d$ -dimensions; and  $\Gamma(1-\beta)$  is the gamma Euler function of  $(1-\beta)$ .

This expression is now used intensively in different heterogeneous systems e.a. in vesicles and on irregular surfaces.<sup>(24,25)</sup>

Before using it on our own systems we want to investigate by a computer simulation study to what extent it is possible to analyse this expression unambiguously.

A fractal decay is hereby simulated and then analysed by different expressions e.a. multi-exponential decay and expressions derived for fluorescence quenching in micellar systems. All of these expressions have been proposed in the past to describe the fluorescence decay of adsorbed molecules.

Also the decays obeying these other expressions will be simulated and then analysed by the expression proposed by Klafter and Blumen.

By using this procedure one can determine if it is possible to distinguish between the different models and find the conditions where this is at best possible.

## 2.2. Method

The simulated decays are obtained by convoluting the decay as predicted by the expressions with a non smoothed measured instrument response function and adding Poisson noise to this. The time increment and the pre-exponential factors are chosen carefully so that the number of counts in the peak channel is about 10,000 and the generated curve decays over at least 2 decades.

The decays are analyzed by a non linear least square method based on the Marquardt algoritme.<sup>(26)</sup> The goodness of fit is evaluated by a number of statistical tests. ( $\chi^2$   $Z\chi^2$  ordinary runs, Durbin Watson ). As a tool for the analysis we use the global analysis program developed in the laboratory. In a global analysis experiment one analyses different decays at the same time taking into account the existing relationships between parameters, based on a model and thus reducing the total amount of parameters. In this way a better precision and an improved modeltesting capability is achieved.

## 2.3. Results

In order to see how accurately the parameters in a decay obeying to the Klafter and Blumen expression can be recovered two sets of experiments were simulated (table 3.) The two sets had values for the fractal dimension  $D=1.75$  ( $\beta=0.292$ ) and  $D=2.95$  ( $\beta=0.485$ ) respectively. Each of the sets consisted out of a number of different decay curves corresponding to different acceptor concentrations.

These simulated decays were then analyzed using the fractal

expression. Parameter  $\tau$  which gives the lifetime of the donor in absence of acceptor molecules was kept constant at his true value during the analysis. (This value can be determined simply by measuring the lifetime of the adsorbed donor molecules in absence of acceptors). Table 4 gives the recovered parameter values, the standard deviation on these parameters and the goodness of fit in the single curve analysis of the simulated decays.

Table 3 : the parameters used to generate the decays

A.  $\beta = 0.295$

$\alpha$	$\tau$	$\gamma[Q]$	$\beta$
50	.333	6	.292
37	.333	5	.292
27	.333	4	.292
18	.333	3	.292
10	.333	2	.292

B.  $\beta = 0.485$

$\alpha$	$\tau$	$\gamma[Q]$	$\beta$
30	.333	6	.485
25	.333	5	.485
20	.333	4	.485
18	.333	3	.485
10	.333	2	.485

table 4 : recovered parameter values with single curve analysis

A.  $\beta = 0.292$

$\alpha$	$\tau$	$\gamma[Q]$	$\beta$	$z\chi^2$
49.92	.333	5.999	.2944	.015
37.01	.333	5.001	.2917	.553
26.75	.333	3.995	.2939	.742
18.18	.333	3.011	.2905	-.921
9.908	.333	1.988	.2934	-.243

B.  $\beta = 0.435$

$\alpha$	$\tau$	$\gamma[Q]$	$\beta$	$z \chi^2$
30.03	.333	6.008	.4854	1.049
24.85	.333	4.998	.4864	-.633
20.94	.333	3.996	.4854	-.018
17.93	.333	3.000	.4876	.054
10.08	.333	2.007	.4814	.937

As can be seen from the data is it possible to extract the parameter values out of the decays with a rather high accuracy and precision. Close examination of the standard deviations on the parameter values reveals a loss of precision as the quencher concentration goes down. Global analysis of the data over the entire quencher concentration region gives an excellent fit and the parameters are recovered with increased accuracy and precision (table 5)

table 5 : recovered parameter values with global analysis

set	$\tau$	$\gamma^*$	$\beta$	$z \chi^2$
A	.333	100.00	.2926	-.243
B	.333	100.01	.4853	.598

(\*)  $\gamma'$  is splitted in the concentration independent  $\gamma$  part and a part which is concentration dependent.  $\gamma$  can then be linked over the whole concentration region.

Analysis of these decays as a mono-exponential decay or a two exponential decay was never possible. The data could be fitted however in single curve analysis to a three-exponential decay (table 6).

table 6 : data fitted to a three-exponential decay (single curve analysis). Synthetic parameters as given in table 3B.

$\alpha$	$\tau$	$\alpha$	$\tau$	$\alpha$	$\tau$	$2\chi^2$
1.169	.420	.902	2.008	.297	6.067	3.037
9.088	.044	8.051	.228	3.477	.713	.945
6.617	.048	7.142	.258	4.130	.857	1.063
4.699	.048	6.167	.289	5.243	1.049	.636
2.478	.118	3.365	.5737	2.993	1.6456	1.069

If we analyze the data globally we have to use a model. Depending on the model we can then take into account different relationships between parameters. e.g. we can link either the decaytimes or the relative contributions of the decay times over a region of concentration. In neither case the data can be fitted globally and we can safely reject the assumed models.

We also tried to analyze the synthetic "fractal" data by the expression used in micellar kinetics :

$$\Phi(t) = A_1 \exp [-A_2 t - A_3(1 - \exp(-A_4 t))]$$

with  $A_2$  : the rateconstant of fluorescence in absence of quencher

$A_3$  : the average number of quenchers in a micel

$A_4$  : the intramicellar quenching rate constant

None of the decays could be fitted to this expression. Very poor fitting and physically unacceptable parameter values were obtained in the whole region of concentrations.

A new set of experiments obeying the equation for micellar kinetics was generated. The synthetic parameter values are shown in table 7. These simulated decays were then analyzed by the "fractal" equation. The returned parameter values and the  $2\chi^2$  value are given in table 8. The lifetime of the unquenched molecule is kept constant on his true value during the analysis. Fitting is rather poor but becomes better as the concentration of quenchers goes down.

table 7 : synthetic parameter values used to simulated the micellar decay.

$A_1$	$A_2$	$A_3$	$A_4$
.12	.05	.2	.936E-02
.13	.05	.5	.936E-02
.13	.05	1	.936E-02
.25	.05	2	.936E-02
.39	.05	5	.936E-02
.90	.05	10	.936E-02

table 8 : obtained parameter values if synthetic "micellar" decays with parameter values as given in table 7 are analyzed by the fractal expression.

$\alpha$	$\tau$	$\gamma[Q]$	$\beta$	$Z\chi^2$
.165	.05	1.253	.2322	34.47
.193	.05	1.169	.2601	90.038
.366	.05	.9988	.3906	192.702
.585	.05	.7005	.3707	403.098
3.25	.05	2.6823	.3411	*****

global analysis of the data gives a unacceptable fit and unrealistic parameter values ( $D > 3$ ).

So even in a single curve analysis one can distinguish between the "fractal" decay and the "micellar" one.

In a last set of experiments we used an expression which is used to analyze energy transfer in monolayers.

$$\Phi(t) = A_1 \exp[-t/\tau_D - q_A(t/\tau_D)^{1/3}] + A_2 \exp(-t/\tau_D)$$

The expression consists out of two parts : one is the generally known expression for Förster energy transfer in two dimensions the other part is a mono-exponential decay. This expression is used to analyze energy transfer in monolayers and is explained by the concept of domain formation in the monolayers.<sup>(27)</sup> The mono-exponential part is then ascribed to the decay of isolated donors far from the acceptors

which reside in an other domain of the monolayer. The mono-exponential decay contributes only for 1% - 3% to the total decay. In table 9 one can find the values that were used to simulate the decays.

table 9 : synthetic parameter values

$A_1$	$\tau_D$	$\gamma$	$A_2$
30	.333	5	.3
30	.333	5	.4
30	.333	5	.5
30	.333	5	.6
30	.333	5	.7
28	.333	5	.8

These decays were fitted then to the fractal expression. The obtained parameter values and goodness of fit is listed in table 10.

table 10 : recovered parameter values and  $Z\chi^2$  value if the simulated decays are analyzed by the fractal expression

$\alpha$	$\tau$	$\gamma$	$\beta$	$Z\chi^2$
44.22	.333	4.561	.2379	93.063
47.78	.333	4.461	.2205	120.929
49.96	.333	4.352	.2069	151.355
52.68	.333	4.273	.1952	174.357
54.95	.333	4.197	.1851	199.651
53.68	.333	4.078	.1721	209.569
54.33	.333	4.087	.1711	207.645

As is clear from the above table one can distinguish rather easily between a fractal behaviour and the expression that one proposes for domain formation as in monolayer systems.

All the above data indicate that the fractal expression is fairly good distinguishable from other expressions for the fluorescence decay. The differences between the expressions become less explicit as the quencher concentration goes down. Using single curve analysis one can fit a fractal decay to a three-exponential function. If the decays are analyzed globally and thus a model is assumed the fits

become unacceptable.



### C. CONCLUSIONS

Cationic detergents adsorb on the clay surface in a non homogeneous way. Spectroscopic evidence for this cluster formation was given in previous reports. At this stage methods are ~~been~~ developed to determine the size of these clusters. Analyzing the fluorescence decay of adsorbed probes with the expression for micellar kinetics seems to be a interesting method. The results obtained by this method will be compared to those obtained by a non-spectroscopic method where one polymerizes the detergent and determines the molecular weight afterwards. Preliminary results give rather small aggregation numbers.

Pyrene probes were adsorbed to the surface of two different colloidal silicas. The charge on the silica surface is pH dependent. This dependence can be seen in the spectroscopic behaviour of the adsorbed probe molecules. At lower pH values the silica particles lose their stability and start to gel. This gelation can be followed spectroscopically.

A simulation study was performed to establish if it is possible to distinguish between a fractal decay as proposed by Klafter and Blumen and other decay functions commonly used on surfaces. As this seems to be the case especially when one analyzes with the aid of the global analysis program one can apply this fractal decay law to experimental data.

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